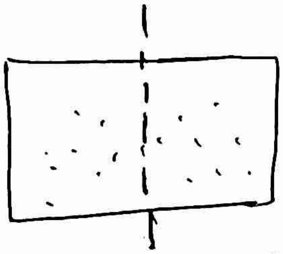
Lecture 5

Recap: Conditions for equilibrium

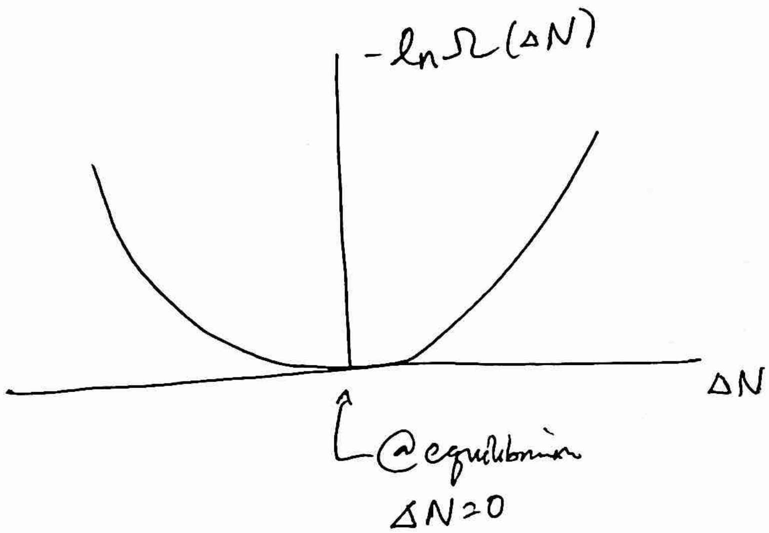


$N_1 + N_2$ total

$N_1 = N_1^{(eq)} + \Delta N \mid N_2 = N_2^{(eq)} - \Delta N$

ΔN: deviation from equilibrium

$\Omega(\Delta N)$: # of microstates given ΔN



$$\left.\frac{d\ln\Omega(\Delta N)}{d\Delta N}\right|_{\text{equilibrium}} = 0$$

We talked about how the logarithm means $\ln\Omega$ is extensive, so

$$\underbrace{\ln\Omega(\Delta N)}_{\substack{\text{\# of states}\\ \text{of combined}\\ \text{system}\\ \text{w/ }\Delta N}} = \underbrace{\ln\Omega_1(N_1^{(eq)}+\Delta N)}_{\substack{\text{\# of states}\\ \text{of left side w/}\\ N_1^{(eq)}+\Delta N\text{ particles}\\ \text{on the left}}} + \underbrace{\ln\Omega_2(N_2^{(eq)}-\Delta N)}_{\substack{\text{\# of states}\\ \text{of right side}\\ \text{w/ }N_2^{(eq)}-\Delta N\\ \text{particles on the right.}}}$$

$$\frac{\partial \ln \Omega(\Delta N)}{\partial \Delta N} = \frac{\partial \ln \Omega_1 (N_1^{(eq)}+\Delta N)}{\partial (N_1^{(eq)}+\Delta N)} \frac{\partial (N_1^{(eq)}+\Delta N)}{\partial \Delta N} + \frac{\partial \ln \Omega_2 (N_2^{(eq)}-\Delta N)}{\partial (N_2^{(eq)}-\Delta N)} \frac{\partial (N_2^{(eq)}-\Delta N)}{\partial \Delta N}$$

$$= \frac{\partial \ln \Omega_1(N)}{\partial N} + \frac{\partial \ln \Omega_2(N)}{\partial N}(-1)$$

$$= \frac{\partial \ln \Omega_1(N)}{\partial N} - \frac{\partial \ln \Omega_2(N)}{\partial N}$$

These are written as partial derivatives because ~~$\Omega(\Delta N)$~~ Ω_1, Ω_2 actually also depend on E + V...

$$\left(\frac{\partial \ln \Omega_1}{\partial N}\right)_{E_1, V_1} = \left(\frac{\partial \ln \Omega_2}{\partial N}\right)_{E_2, V_2}$$

If these derivatives were not equal, more particles would flow from one side to the other until the partial derivatives were equal.

$\boxed{E_1}$ $\boxed{E_2}$ $\longrightarrow$ $\boxed{E_1 + E_2}$

Energy won't stop flowing until

$$\left(\frac{\partial \ln \Omega_1}{\partial E}\right)_{N_1, V_1} = \left(\frac{\partial \ln \Omega_2}{\partial E}\right)_{N_2, V_2} \qquad (\beta_1 = \beta_2)$$

This is exactly what we expect of our everyday notion of temperature!

Energy will flow until the temperatures are equal.

We could have tried to define β as temperature, but energy flows from low β to high β. We want energy to flow from high temperature to low, so

$$\left(\frac{\partial \ln \Omega_1}{\partial E}\right)_{N,V} \propto \frac{1}{T_1} \leftarrow \text{Temperature of system 1}$$

$$\left(\frac{\partial \ln \Omega}{\partial E}\right)_{N,V} \propto \frac{1}{T_2} \leftarrow \text{Temperature of system 2}$$

What are the units of that proportionality constant?

$$\left(\frac{\partial \ln \Omega_1}{\partial E}\right)\begin{matrix}\leftarrow \text{unitless}\\ \leftarrow \text{energy}\end{matrix} = \frac{1 \leftarrow \text{unitless}}{\underset{\uparrow\ \frac{\text{energy}}{\text{degree}}}{k_B}\, T_1 \leftarrow \text{degrees}}$$

k_B is essentially a unit conversion!

$$\Rightarrow \left(\frac{\partial\,(k_B \ln \Omega)}{\partial E}\right)_{N,V} = \frac{1}{T}$$

Lets give this a name

$$S = k_B \ln \Omega \quad \Leftarrow \text{Boltzmann's entropy}$$

1. Since $\Omega = \omega^N \Rightarrow S = k_B \ln \omega^N = N k_B \ln \omega$

$\Rightarrow S$ is extensive.

2. Gibbs had a more general definition of entropy:

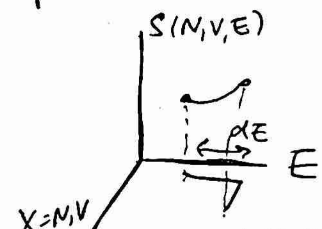
$$S = -k_B \sum_{\nu} P(\nu) \ln P(\nu)$$

There is a minus sign here, but no minus sign on Boltzmann's entropy. On your problem set you'll see that the Gibbs entropy is the same as the Boltzmann entropy when $P(\nu)$ is uniform.

3. What is S a function of?

$$S(N,V,E) = k_B \ln \Omega(N,V,E)$$

Entropy is a multivariable function that counts – on an exponential scale – how many microstates are possible as a function of the (rigid) constraints.



The chain rule gives:

$$dS = \underbrace{\left(\frac{\partial S}{\partial E}\right)_{N,V}}_{\boxed{\frac{1}{T}}} dE + \left(\frac{\partial S}{\partial V}\right)_{E,N} dV + \left(\frac{\partial S}{\partial N}\right)_{V,E} dN$$

These two get special names too!